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TRANSLATION

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By

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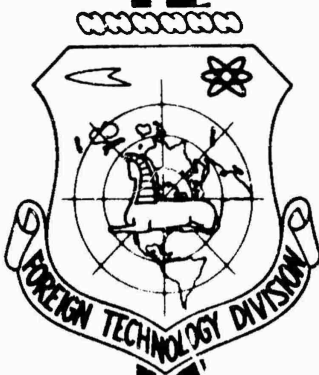
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IGNITABILITY OF ALLOYS OF THE ZIRCONIUM-TITANIUM SYSTEM*

V. G. Ioffe

Studying the ignitability of zirconium alloys with titanium represents interest in view of the absence of published data about the ignitability of systems with unlimited mutual solubility of components in solid state.

The process of preparing samples consisted of the following operations: arc melting in argon atmosphere, crushing, hydrogenation at 800°, pulverization in a mortar to dimensions of < 53 microns, dehy-

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*Work was done under the leadership of Professor B. M. Zlobinskiy.

drogenation in vacuum 10^{-4} mm mercury column at 800°. Pulverization and storage of samples was carried out in the air without the use of any measures for the prevention of surface oxidation in order to bring closer the burning properties of the investigated powders to the properties of dust, forming during cold machining of metal under industrial conditions.

Temperature of spontaneous ignition of the alloys and compounds were determined at the installation, described in [1 - 3]. Spontaneous combustion temperatures of alloys are given in table, and for certain zirconium compounds with metalloids, they were found to be equal; for zirconium hydride 282°, for carbide 430°, for nitride 585°, and for boride 660°. It is known that the dependence of ignition, temperature upon the composition of the mixture of two mutually soluble burning liquids represents a smooth curve with downward bending [4]. Results of this investigation show that this rule spreads also to solid solutions of zirconium with titanium. When comparing the obtained ignitability diagram with the diagram of state (Fig. 1 and 2a), it appears to be possible to represent the ignitability curve as a sum of the two functions: linear, describing the rise in temperature in ratic of increasing the content in the alloy of less burning component, and curvilinear, approximately reproducing the liquidus lines of the diagram of state. In this way, an analytical ignition curve can be described by equation

$$t_{\text{в}} \approx t_{\text{п}} + ac - b, \qquad (1)$$

where t_V - temperature of autoignition of the alloy.

Table

Experimental $t_в^3$ and calculated $t_в^P$ of auto ignition temperature of the alloys

Ti — Mn, $t_в^P = t_n + 3{,}65c - 1025$

Content Mn, %	0	1,2	2	3,1	5,1	6	10,2	19,8	31,2	40,8	50,5	60,6	71,2	79,6	91
$t_в^3$	635	610	630	660	655	650	680	630	505	330	370	480	505	460	530
$t_в^P$	635	635	624	618	617	611	589	520	434	350	436	510	610	616	580
$t_в^P - t_в^3$	0	—5	—6	—42	—38	—39	—91	—110	—71	0	+66	+60	+45	+156	0
$[(t_в^P - t_в^3):(t_в^3+273)]100$	0	—0,5	—0,7	—4,5	—4,1	—4,2	—9,5	—12,2	—9,1	0	+10,5	+8,0	+5,9	+21,3	0

Ti — Al, $t_в^P = t_n + 8{,}29c - 1085$

Content Al, %	0	1	2,1	3	4,5	6	10,6	20	29,6	40,2	50	61,5
$t_в^3$	635	660	655	670	670	680	730	720	790	810	790	785
$t_в^P$	635	638	642	645	652	660	663	696	700	704	755	785
$t_в^P - t_в^3$	0	—22	—13	—25	—18	—20	—67	—24	—90	—106	—35	0
$[(t_в^P - t_в^3):(t_в^3+273)]100$	0	—2,4	—1,4	—2,6	—1,9	—2,1	—6,7	—2,4	—8,5	—9,8	—3,3	0

Zr — Si, $t_в^P = t_n + 14{,}4c - 1592$

Content Si, %	0	4,65	7,19	13	17,3	18,8	20,4	24	37	46	59	75
$t_в^3$	253	276	287	350	490	577	503	510	600	772	838	845
$t_в^P$	253	125	442	785	878	1019	1052	854	731	591	708	845

Zr — Ti, $t_{\text{н}}^{\text{p}} = t_{\text{n}} + 5c - 1592$

Content Ti %	0	23,7	26,4	52,4	64,1	76	87,9	100
$t_{\text{в}}^{\text{в}}$	253	273	297	334	35`	408	597	653
$t_{\text{в}}^{\text{p}}$	2?3	253	263	278	375	465	5(0	653
$t_{\text{н}}^{\text{p}} - t_{\text{в}}^{\text{в}}$	0	—20	—34	—56	+17	+57	—37	0
$[(t_{\text{в}}^{\text{p}} - t_{\text{в}}^{\text{в}}) : (t_{\text{в}}^{\text{в}} + 273)]\,100$	0	—3,7	—6,0	—9,2	+2,7	+8,4	—4,2	0

Ti — Si, $t_{\text{в}}^{\text{p}} = t_{\text{n}} + 2,53c - 1052$

Content Si %	0	4,9	10,2	21	29,7	40,5	51,2	60
$t_{\text{в}}^{\text{в}}$	635	500	450	460	520	540	560	600
$t_{\text{в}}^{\text{p}}$	635	400	394	901	1123	900	568	600

Remarks: 1. Melting point of alloys found by various liquiduses of the diagram of state from [5 - 8]. For the Zr—Ti system for a melting point was accepted a mean arithmetical between temperatures of the liquidus and solidus. 2. Alloy 87.6% Zr + 12. 4% Ti was ignited during the pulverization of the hydride.
3. Content of metal is given in weight percentages.

tn – melting point of alloy; c – content of titanium in alloy (in unitary fractions).

Constant a and b can be found from equation (1) if the t_p and t_v values are known for any two compositions of the alloy. Having replaced these values in equation (1) and having solved the system relative to a and b, we obtain

$$a = \frac{\theta_1 - \theta_2}{c_2 - c_1}, \qquad (2)$$

$$b = \theta_1 - c_1 \frac{\theta_1 - \theta_2}{c_1 - c_2} = \theta_2 \div c_2 \frac{\theta_1 + \theta_2}{c_2 - c_1}, \qquad \cdot(3)$$

where $\theta = t_p - t_v$, and indices 1 and 2 show that the given value pertains to one of the two alloys with known autoignition temperature and
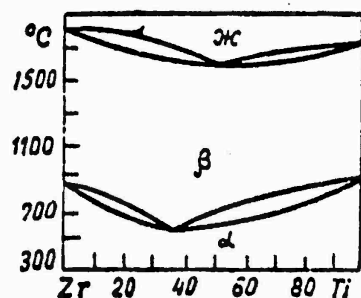
titanium content c_1 or c_2.

Fig. 1. Diagram of
state of system Zr-Ti.

In some special

cases, formulas (2)

and (3) acquire a more

simple way.

The special case

1: $c_1 = 0$, $c_2 = 1$ (known

t_p and t_v for pure alloy

components). Then a =

$\theta_1 - \theta_2$, b = θ_1.

Fig. 2. Experimental
(1) and calculated
(2) ignition diagrams
of the system: Zr-Ti
(a); Zr-Si (b), Ti-Al
(v); Ti-Mn (g), Ti-Si
(d).

Special case 2: $c_1 \neq 0$, $C_2 = 1$. Then a = $\dfrac{\theta_1 - \theta_2}{c_2}$, b = θ_1.

In order to explain how much general character equation (1) has,

calculations were made of auto ignition temperatures not only for system

Zr-Ti, but also for systems: Ti-Al, Ti-Mn, Ti-Si, and Zr-Si. Results

of calculations (se table) reveal a satisfactory coincidence with ex-

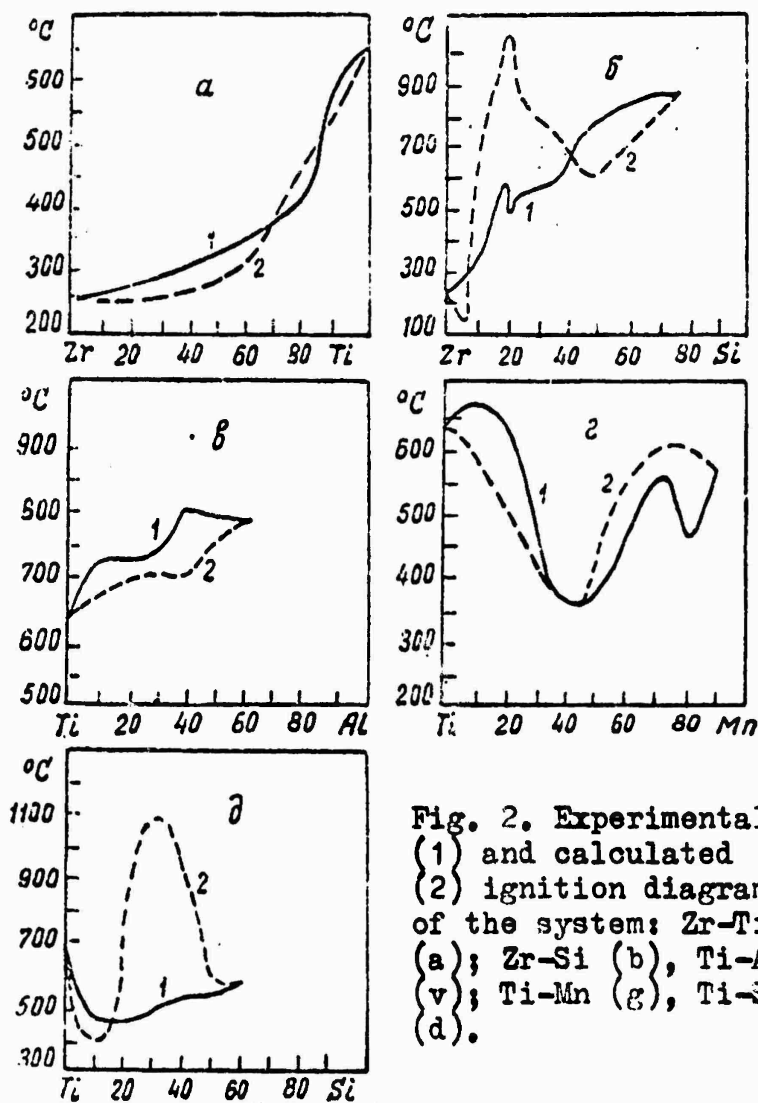perimental data for systems Zr-Ti, Ti-Al, and Ti-Mn. This shows that

for the enumerated systems, the change in autoignition temperatures of alloy in comparison with autoignition temperatures of pure components depends, first of all, upon the melting point which can be explained on the basis of metal combustion mechanisms with the solution of the protective oxide layer [3].

For Ti-Si and Zr-Si systems, there is observed a greater discrepancy of data with experimental (see Fig. 2) and it is possible to detect a qualitative relationship between ignition and state diagrams. It is apparent that the autoignition temperature of alloys containing silicon, in addition to the melting point of the alloy, also affect with another or with other factors. One of these, most likely, appears to be the formation of silicides because in regions of the diagram corresponding to difficulty melting compounds Ti_5Si_3 and Zr_6Si_5, a sharp rise is observed in calculated autoignition temperature, considerably exceeding the experimental data. Furthermore, it should be taken into consideration that the composition of the oxide film, through which oxygen is diffused during oxidation in the period before inflammation, does not always correspond to the composition of the alloy. To explain this phenomenon, it is necessary to make a further investigation. The degree of autoignition temperature, depending upon the melting point of the alloy, can be evaluated by the coincidence of calculated and experimental autoignition temperature values.

Visual observation of the combustion of the powder layer reveals that combustion of metal powders is possible in the form of smoldering and in the form of ignition. During the smoldering, the incandescence,

the red hot combustion zone, moves closely from the place of initiation. During ignition, the powder gets hot to a very high brightness and burns very brightly, spilling in the initial moment the hot particles. The reaminder of the powder after incandescence - fast, after the incandescence - caked.

These forms of combustion are distinguished by an oxygen transfer mechanism. During the incandescence, temperature is insufficient for the appearance of liquid phase because the outer layer of the powder looses too much heat and the internal layers burn at insufficient oxygen. The oxygen is diffused through the oxide layer, as during ordinary high temperature corrosion, but diffusion becomes facilitated by the oxide film in the metal.

Smoldering can change into conflagration as a result of self heating or during the loosening of the layer. In this case, as a result of temperature increase on the surface of the metal appears a liquid phase, dissolving the protective oxide layer. Initially, the liquid phase probably appears in places of disrupting the solidity of oxide layer, originating at polymorphous transformations of oxide with the change in volume. The surface of the metal is denuded and the reaction accelerates.

At the combustion method adopted in this report, as a rule, it takes place in the form of smoldering.* During the smoldering, no liquid

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*Conflagration is undesirable because the used apparatus does not stand any developing temperatures thereat.

phase is formed but the beginning of smoldering temperature, as shown by experimental results, sharply depends upon the melting point. This speaks about the thing that during the reduction in melting poin. is also reduced the temperature, at which the rate of oxygen diffusion becomes sufficient for the beginning of smoldering.

Conclusions

1. Determined experimentally were the autoignition temperature of zirconium with titanium alloys and an ignition diagram of the Zr-Ti system was formulated.

2. Found was an approximate expression of the autoignition temperature dependence of the alloy upon its composition and it was established that Zi-Ti, Ti-Al, and Ti-Mn systems satisfactorily submit to that dependence.

3. Ignition of Zr-SI and Ti-Si alloys deviates sharply from the found dependence which is presumably explained by the formation of high melting silicides.

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